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RAMAN SPECTRA OF FLUOROBENZENE AT DIFFERENT LOW TEMPERATURES

DEB KUMAR MUKHERJEE

OPTICS DEPARTMENT, INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE, CALCUTTA 32

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Plate VII

ABSTRACT. The Raman spectra of fluorobenzene in the solid state at −60°C and at −180°C have been investigated and compared with the spectrum due to the liquid. At −60°C the crystals produce a new low-frequency line at 95 cm^{-1} and the line shifts to 100 cm^{-1} when the temperature is lowered to −180°C. This new line has been attributed to the formation of dimers at low temperature. Further, the Raman shifts of some prominent lines have been observed to change with solidification of the compound and lowering of temperature and these changes also have been attributed to the formation of dimers.

The polarisation of the Raman lines of the compound has been reinvestigated and it has been observed that the line 517 cm^{-1} is not totally depolarised and although the value of factor of depolarisation is quite large it is actually less than 6/7.

INTRODUCTION

The Raman spectra of many mono- and disubstituted benzenes in the solid state at different low temperatures were studied by many previous workers. The Raman spectra of chlorobenzene and bromobenzene studied earlier by Ray (1950) and Biswas (1955) respectively showed that in the spectrum of frozen chlorobenzene at −60°C there are five new lines in the low frequency region the intensities and frequency-shifts of which increase when the temperature is lowered to −180°C. In the case of crystalline bromobenzene at −60°C only two new lines appear in the low frequency region while the number increases to three with lowering of temperature to −180°C. These results were interpreted on the hypothesis that the lines are due to small groups of molecules formed through virtual linkages in the solid state and the changes with temperature were attributed to the strengthening of these bonds and formation of fresh bonds at lower temperatures. The fluorobenzene molecule contains a highly active fluorine atom and the behaviour of this molecule in the solid state was not known. The Raman spectra of this compound at −60°C and at −180°C have, therefore, been investigated to find out the number of new low-frequency lines which may be produced by this compound in the solid state and the dependence of intensity and positions of the lines on temperature.

As regards the assignment of the Raman lines to different modes of vibration of the molecule as given in the Tables by Landolt-Börnstein (1951) the line 518 cm^{-1} has been assigned to a totally symmetric mode but the line has been described as a totally depolarised one. This is anomalous and therefore the polarisation of the Raman lines of this compound has been re-investigated to find out whether the discrepancy is genuine or not.

EXPERIMENTAL

Chemically pure sample of fluorobenzene obtained from Eastman Organic Chemicals Co of New York was used in the present investigation and it was repeatedly distilled under reduced pressure before each exposure. The Raman spectra due to the substance in the liquid state and in the solid state at $-60°C$ and at $-180°C$ were photographed with the arrangements used by previous workers in this laboratory (Biswas, 1954). The intermediate temperature of $-60°C$ was obtained by using as a refrigerant a mixture of alcohol and liquid oxygen in proper proportion in a Dewar vessel of Pyrex glass All the Raman spectra were photographed on Ilford Zenith plates using a Fuess glass spectrograph giving a dispersion of about 11 A per mm in the 4000 Å region. Iron arc spectrum was also recorded on each spectrogram as comparison

In order to study the polarisation of the Raman lines light from two horizontal mercury arcs was focussed with cylindrical condensers on the horizontal pyrex glass tube containing the liquid and the two components of the scattered light were focussed on the slit of the spectrograph one above the other with the help of a double image prism With this arrangement the convergence of the incident light made the horizontal component of the totally depolarised line more intense than the vertical component So, it was easy to find out the totally depolarised lines in the spectrum.

RESULTS AND DISCUSSION

Spectrograms showing the Raman lines due to fluorobenzene in the liquid state and in the solid state at different temperatures are reproduced in Figs. 1(a)–1(c) and the polarised Raman spectrum of the liquid is shown in Fig 1(d), Plate V II The low frequency line due to the solid at $-60°C$ and $-180°C$ is shown in the enlarged spectrograms in Figs. 2(a) and 2(b) respectively in the same plate.

The Raman frequencies due to the substance in the liquid and solid states are given in Table I. The Raman shifts due to the liquid reported by previous workers (Magat, 1936) are also given in the same table for comparison.

(*a*) *New Raman lines in the low frequency region*

It can be seen from Figures 2(a) and 2(b) and from Table I that only one broad new line at 95 cm^{-1} appears in the Raman spectrum due to the frozen fluorobenzene at $-60°C$, and the line becomes sharper and is shifted to 100 cm^{-1} when

TABLE I

Fluorobenzene, C_6H_5F

$\Delta\nu$ in cm^{-1}

Liquid		Solid	
Magat, 1936	Present author at 30°C	at −60°C	at −180°C
		95 (7b) o, k	100 (7) o, k
243 (8) 6/7	242 (8b)±o, k , D	255 (5) o, k	260 (2) o, k
424 (1)			
500 (0)			
518 (3) 6/7	517 (3) o, k ; P	510 (0) o, k	510 (1b) o, k
615 (2) 6/7	615 (2) o, k ; D	615 (0) o, k	615 (1b) o, k
705 (1)			
755 (1)	755 (1) o, k		
806 (9) 0,5	806 (6) o, k ; P	806 (5) o, k	806 (6) o, k
830 (1)			
883 (0) 6/7			
997 (2)	998 (1) o, k	996 (4) o, k	996 (5) o, k
1010 (10) 0,1	1009 (10) o, k ; P	1010 (4) o, k	1010 (4) o, k
1025 (1)			
1068 (1)	1068 (ob) o, k		
1157 (3) 6/7	1158 (4) o, k , D	1158 (0) o, k	1158 (1) o, k
1220 (4) 0,5	1222 (3) o, k ; P	1214 (1) o, k	1214 (3) o, k
1280 (0)			
1413 (0)			
1498 (1)	1499 (2) o	1499 (0) o	1499 (1) o
1601 (4) 6/7	1602 (3b) o, k ; D	1603 (0b) o	1603 (1b) o
1625 (0)	1625 (0) o, k		
2615 (1)			
2917 (1)			
2986 (1)	2990 (0) k ?		
3027 (1)			
3074 (10) 0,1	3075 (12b) o, k , P	3082 (5b)	3088 (7b) k
3090 (–)			
3180 (–)			
3677 (–)			

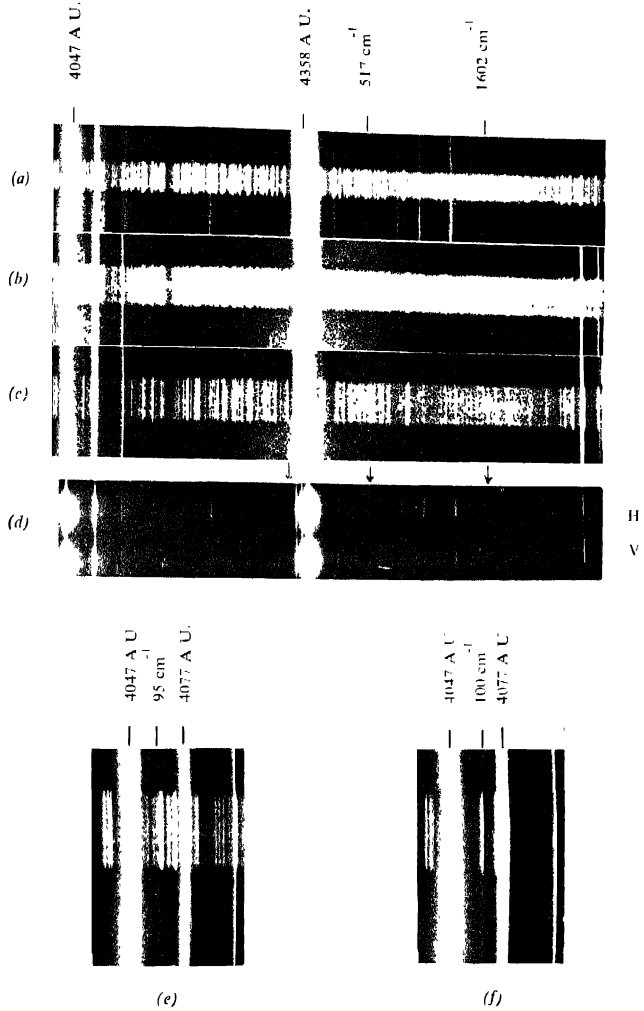

Fig. 1. Raman spectra of fluorobenzene

(a) Liquid at 30°C
(b) Solid at −60°C
(c) Solid at −180°C
(d) Polarisation of Raman lines
(e) Showing low frequency Raman lines at −60°C
(f) Showing low frequency Raman lines at −180°C

the temperature is further lowered to −180°C. The changes in the Raman shifts of the low frequency lines due to chlorobenzene and bromobenzene were reported previously by Ray (1950) and Biswas (1955) respectively. Ray (1950) observed five new lines in the case of chlorobenzene in the solid state both at −60°C and −180°C, while bromobenzene showed (Biswas, 1955) two such lines at −60°C and three new lines at −180°C. The crystal structures of the compounds were not known at that time but recently Biswas (1958) has reported that both the crystals of chlorobenzene and bromobenzene at −180°C belong to the same space group Q_h^{13} and also contain the same number of molecules per unit cell. If the new lines were due to lattice oscillations depending on the symmetry of the lattice the number of such lines would be the same in both these cases, but actually it is not so. The space group of fluorobenzene crystals is not known but the fact that other monosubstituted benzenes produce more than one line in the solid state while only one new line is observed in the case of fluorobenzene cannot be explained by the hypothesis put forward by Bhagavantam (1941) and Kastler and Rousset (1941) independently that angular oscillations of the molecules pivoted in the crystal lattice give rise to these new lines. Moreover, the amplitude of angular oscillation would decrease and consequently the intensity of the new line would diminish at lower temperatures, but actually the intensity of the line does not diminish with lowering of temperature from −60°C to −180°C.

Ray (1950) and Biswas (1955) concluded from the changes observed in the intensities and frequency-shifts of the low frequency lines in the case of crystals of chlorobenzene and bromobenzene respectively with lowering of temperature of the crystals that these lines might be due to oscillations in groups of molecules formed by virtual intermolecular linkages in the solid state as proposed by Sirkar (1936). Kastha (1958) recently found evidence of formation of such groups even in the liquid state just above the freezing point. The replacement of a bromine atom by the chlorine atom in the benzene ring may appreciably increase the affinity of the molecule to form intermolecular linkages with more distant neighbours increasing thereby the size of the associated groups and the number of the new Raman lines given by such groups. The situation is different in the case of fluorobenzene because fluorine being more reactive than chlorine the molecules may form dimers even in the liquid state just above the freezing point with a structure of the dimer in which the fluorine atom of each of the two molecules is attached to a hydrogen atom of the other molecule.

(*b*) *Shift of Raman lines of the molecule with solidification*

Table I shows that most of the Raman frequencies reported by Magat (1936) in the case of fluorobenzene in the liquid state have been observed in the present investigation. The line 242 cm^{-1} due to the liquid is found to shift to 255 cm^{-1} when the liquid is frozen and the temperature is lowered to −60°C and to 260 cm^{-1} at −180°C. The line 517 cm^{-1} shifts to 510 cm^{-1} when the liquid is frozen and

cooled to −180°C. The spectrum due to the liquid shows a feeble line with Raman shift 998 cm^{-1} and an intense line 1009 cm^{-1}. The line 998 cm^{-1} shifts to 996 cm^{-1} and becomes stronger with the solidification of the liquid and lowering of temperature to −60°C. This can be explained on the assumption that the line 996 cm^{-1} is due to dimers the number of which increases with solidification of the liquid. The line 1222 cm^{-1} observed in the liquid is shifted to 1214 cm^{-1} when the liquid is solidified. Further the Raman line 3075 cm^{-1} shifts to 3082 cm^{-1} with the solidification of the liquid and to 3088 cm^{-1} when the crystal is further cooled to −180°C.

On comparing the results with those due to bromobenzene(Biswas, 1955) it is found that the line 242 cm^{-1} of fluorobenzene behaves in the same way with solidification of the liquid and lowering of temperature as the line 182 cm^{-1} of bromobenzene. Biswas assigned the latter line to the vibration of type corresponding to the c_u^+ mode of the benzene ring given in Figure 1, No. 16 by Sponer and Kirby-Smith (1941) and the shift was attributed to the formation of virtual linkages between neighbouring molecules. In the present case also similar explanation holds good. The shift of the other lines mentioned above also lend support to the hypothesis that dimers are formed in the solid state of the substance.

(*c*) *Polarisation of the line* 517 cm^{-1}

The polarised Raman spectrum of liquid fluorobenzene shows that the horizontal component of the totally depolarised line 1602 cm^{-1} is more intense than the vertical component while the vertical component of the 517 cm^{-1} line is slightly more intense than the horizontal component. Hence the latter line is not totally depolarised and although the value of factor of depolarisation is quite large it is certainly less than 6/7.

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